(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 4 043 591 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
17.08.2022 Bulletin 2022/33

(21) Application number: **20904807.3**

(22) Date of filing: **20.11.2020**

(51) International Patent Classification (IPC):
C21D 8/10 $^{(2006.01)}$ ***C21D 9/08*** $^{(2006.01)}$
C22C 38/00 $^{(2006.01)}$ ***C22C 38/58*** $^{(2006.01)}$

(52) Cooperative Patent Classification (CPC):
C21D 9/08; C22C 38/00; C22C 38/58; C21D 8/10

(86) International application number:
PCT/JP2020/043310

(87) International publication number:
WO 2021/131445 (01.07.2021 Gazette 2021/26)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
KH MA MD TN

(30) Priority: **24.12.2019 JP 2019232430**

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(54) HIGH-STRENGTH STAINLESS STEEL SEAMLESS PIPE FOR OIL WELLS

(57) To provide a high-strength seamless stainless steel pipe for oil well that has high strength, is excellent in hot workability, has excellent carbon dioxide gas corrosion resistance, and is excellent in SSC resistance under a low temperature environment. A high-strength seamless stainless steel pipe for oil well having a composition containing the particular components, the balance being Fe and unavoidable impurities, and satisfying the following expression (1) and the following expression (2), having a number density of an inclusion having a major axis of 5 μm or more and $0.5 < \mathrm{Ti}/(\mathrm{Ti}+\mathrm{Al}+\mathrm{Mg}+\mathrm{Ca}) < 1.0$ of 0.5 per mm^2 or more and 3 per mm^2 or less, and having a yield strength of 655 MPa or more, wherein in $0.5 < \mathrm{Ti}/(\mathrm{Ti}+\mathrm{Al}+\mathrm{Mg}+\mathrm{Ca}) < 1.0$, Ti, Al, Mg, and Ca represent the contents (% by mass) of the elements in the inclusion, and an element that is not contained is designated as 0,

$$\mathrm{Cr}+0.65\mathrm{Ni}+0.6\mathrm{Mo}+0.55\mathrm{Cu}-20\mathrm{C} \geq 15.0 \quad (1)$$

$$\mathrm{Cr}+\mathrm{Mo}+0.3\mathrm{Si}-43.3\mathrm{C}-0.4\mathrm{Mn}-\mathrm{Ni}-0.3\mathrm{Cu}-9\mathrm{N} \leq 11.0 \quad (2)$$

wherein Cr, Ni, Mo, Cu, C, Si, Mn, and N represent the contents (% by mass) of the elements, and an element that is not contained is designated as 0.

Description

Technical Field

[0001] The present invention relates to a seamless stainless steel pipe that is favorably used in an oil well or a gas well of crude oil or natural gas (which may be hereinafter referred simply to as an oil well) and the like. In particular, the present invention relates to a seamless stainless steel pipe that is excellent in carbon dioxide gas corrosion resistance under an extremely severe corrosive environment containing carbon dioxide gas (CO_2) and chloride ion (Cl^-) at a high temperature of 150°C or more and in SSC resistance under a low temperature environment.

Background Art

[0002] In view of the sharp rise in crude oil price and the depletion of oil resources expected in the near future, high-depth oil wells and oil wells and gas wells with a severe corrosive environment under the so-called sour environment containing hydrogen sulfide and the like, which have not been addressed, are being actively developed in recent years. These oil wells and gas wells generally have an extremely high depth, and the environment thereof is at high temperature and is a severe corrosive environment containing CO_2 and Cl^- and also containing H_2S. A steel pipe for oil well used under the environment is demanded to have a material property that has both intended high strength and excellent corrosion resistance.

[0003] In oil wells and gas wells under an environment containing carbon dioxide gas (CO_2), chloride ion (Cl^-), and the like, a 13Cr martensitic stainless steel pipe has been frequently used as an oil well pipe for oil drilling. Recently, there is an increasing use of an improved 13Cr martensitic stainless steel pipe obtained by decreasing C and increasing Ni, Mo, and the like of the 13Cr martensitic stainless steel pipe.

[0004] For example, PTL 1 describes a martensitic stainless steel containing, in terms of % by mass, C: 0.010-0.030%, Mn: 0.30-0.60%, P: 0.040% or less, S: 0.0100% or less, Cr: 10.00-15.00%, Ni: 2.50-8.00%, Mo: 1.00-5.00%, Ti: 0.050-0.250%, V: 0.25% or less, N: 0.07% or less, and at least one of Si: 0.50% or less and Al: 0.10% or less, the balance being Fe and impurities, satisfying the expression (1), $6.0 \leq Ti/C \leq 10.1$, and having a yield strength of 758 to 862 MPa.

[0005] PTL 2 describes a production method of a martensitic seamless stainless steel pipe, including subjecting a martensitic stainless steel having a composition containing, in terms of % by mass, C: $\leq$ 0.050, Si: $\leq$ 0.5, Mn: $\leq$ 1.5, P: $\leq$ 0.03, S: $\leq$ 0.005, Cr: 11.0-14.0, Ni: 4.0-7.0, Mo: 1.0-2.5, Cu: 1.0-2.5, Al: $\leq$ 0.05, and N: 0.01-0.10, the balance being Fe and unavoidable impurities to hot working, then to a heat treatment including cooling to a temperature of the Ms point or less, then heating to a temperature T of 550°C or more and Ac_1 or less at an average heating rate of from 500 to T°C of 1.0°C/sec or more, and then cooling to a temperature of the Ms point or less.

[0006] PTL 3 describes a high-strength martensitic stainless steel excellent in stress corrosion cracking resistance containing C: 0.06% or less, Cr: 12-16%, Si: 1.0% or less, Mn: 2.0% or less, Ni: 0.5-8.0%, Mo: 0.1-2.5%, Cu: 0.3-4.0%, and N: 0.05% or less, having an area ratio of a δ-ferrite phase of 10% or less, and having a fine precipitate of Cu dispersed in the matrix.

Citation List

Patent Literatures

[0007]

PTL 1: WO 2008/023702
PTL 2: JP-A-9-170019
PTL 3: JP-A-7-166303

Summary of Invention

Technical Problem

[0008] Associated with the recent development of oil wells, gas wells, and the like under a severe corrosive environment in recent years, the steel pipe for oil well is being demanded to have both high strength and excellent carbon dioxide gas corrosion resistance under a severe corrosive environment at a high temperature of 150°C or more containing CO_2 and Cl^-. In addition, associated with the development environment becoming severe, the steel pipe is demanded to have excellent SSC resistance under a low temperature environment, such as deep sea.

[0009] However, the techniques described in PTLs 1 to 3 are insufficient in SSC resistance under a low temperature environment although the high strength and the excellent carbon dioxide gas corrosion resistance are achieved.

[0010] Under the circumstances, an object of the present invention is to solve the problems of the conventional techniques and to provide a high-strength seamless stainless steel pipe for oil well that has high strength, is excellent in hot workability, has excellent carbon dioxide gas corrosion resistance, and is excellent in SSC resistance under a low temperature environment.

[0011] The "high-strength" referred herein means that a yield strength YS of 95 ksi (655 MPa) or more is achieved.

[0012] The excellent carbon dioxide gas corrosion resistance means that the corrosion rate is 0.125 mm/y or less in the case where a test specimen is immersed in a test solution, i.e., a 20% by mass NaCl aqueous solution (solution temperature: 150°C, CO_2 gas atmosphere of 10 atm), retained in an autoclave, for an immersion time of 14 days.

[0013] The "excellent SSC resistance under a low temperature environment" means that no crack is formed in a test specimen after subjecting to the test of immersing the test specimen in an aqueous solution having pH of 4.5 which is obtained by adding Na acetate and hydrochloric acid to a test solution, i.e., a 25% by mass NaCl aqueous solution (liquid temperature: 4°C, H_2S: 0.1 bar, CO_2: 0.9 bar) for an immersion time of 720 hours, while applying thereto a load stress of 90% of the yield stress.

Solution to Problem

[0014] For achieving the object, the present inventors have investigated an influence on the low temperature SSC resistance of stainless steel pipes of various compositions. As a result, it has been found that all SSC in the stainless steels occurs from pitting corrosion as the initiation site. As a result of the investigation on the occurrence of the pitting corrosion, it has been found that an oxide or a sulfide containing Al, Ca, Mg, and the like as a major component among various inclusions most tends to be the initiation site of the pitting corrosion under a low temperature environment. Accordingly, for enhancing the SSC resistance under a low temperature environment, it is important to decrease as far as possible the oxide based or sulfide based inclusion containing Al, Ca, Mg, and the like as a major component. However, the oxide based inclusion and the sulfide based inclusion are formed with oxygen and sulfur contained as impurities in the steel, and therefore are impossible to be avoided completely industrially. In view of the situation, there occurs an idea of detoxification of the oxide based inclusion and the sulfide based inclusion through structural change thereof. Specifically, it has been found that the SSC resistance under a low temperature environment can be enhanced by covering the inclusion, which tends to be pitting corrosion, with TiN to prevent the inclusion from becoming the initiation site of pitting corrosion. It is considered that the phenomenon is caused in such a mechanism that in the case where the inclusion is covered with TiN, in dissolving the inclusion, N ion is released to the solution and changed to NH^{3+}, which locally increases the pH in the vicinity of the inclusion to inhibit the occurrence and growth of the pitting corrosion.

[0015] The present inventors have also investigated the influence of the microstructure of steel on the low temperature SSC resistance. As a result, it has been found that under a low temperature environment, the growth of pitting corrosion and the occurrence of cracks can be suppressed to enhance the SSC resistance, by decreasing the prior austenite grain diameter. It is considered that the phenomenon is caused in such a mechanism that P and S segregated on the prior austenite grain boundary (1) accelerate the selective dissolution of the austenite grain boundary in the growth of pitting corrosion, and (2) accelerate the embrittlement of the grain boundary in the invasion of hydrogen into the steel. It is considered that with a smaller prior austenite grain diameter, the grain boundary area per unit volume of steel becomes larger, and thus the concentration of P and S segregated on the prior austenite grain boundary is decreased to enhance the SSC resistance. The mechanism of the conspicuous influence of the prior austenite grain boundary on the SSC resistance under a low temperature environment is considered that the solubility of hydrogen sulfide, which accelerates the invasion of hydrogen to the steel, in the test solution is increased, and the gasification of hydrogen is suppressed by the decrease of the temperature.

[0016] The present invention has been completed based on the findings and the further investigations made thereon. The substance of the present invention is as follows.

[1] A high-strength seamless stainless steel pipe for oil well having a composition containing, in terms of % by mass,

C: 0.002-0.05%,
Si: 0.05-0.50%,
Mn: 0.04-1.80%,
P: 0.030% or less,
S: 0.002% or less,
Cr: 11.0-14.0%,
Ni: 3.0-6.5%,
Mo: 0.5-3.0%,

Al: 0.005-0.10%,
V: 0.005-0.20%,
Ti: 0.01-0.20%,
Co: 0.01-1.0%,
N: 0.002-0.15%, and
O: 0.010% or less,

the balance being Fe and unavoidable impurities, and satisfying the following expression (1) and the following expression (2),

having a number density of an inclusion having a major axis of 5 μm or more and $0.5 < \mathrm{Ti}/(\mathrm{Ti}+\mathrm{Al}+\mathrm{Mg}+\mathrm{Ca}) < 1.0$ of 0.5 per mm^2 or more and 3 per mm^2 or less, and having a yield strength of 655 MPa or more,

wherein in $0.5 < \mathrm{Ti}/(\mathrm{Ti}+\mathrm{Al}+\mathrm{Mg}+\mathrm{Ca}) < 1.0$, Ti, Al, Mg, and Ca represent the contents (% by mass) of the elements in the inclusion, and an element that is not contained is designated as 0,

$$\mathrm{Cr}+0.65\mathrm{Ni}+0.6\mathrm{Mo}+0.55\mathrm{Cu}-20\mathrm{C} \geq 15.0 \qquad (1)$$

$$\mathrm{Cr}+\mathrm{Mo}+0.3\mathrm{Si}-43.3\mathrm{C}-0.4\mathrm{Mn}-\mathrm{Ni}-0.3\mathrm{Cu}-9\mathrm{N} \leq 11.0 \qquad (2)$$

wherein Cr, Ni, Mo, Cu, C, Si, Mn, and N represent the contents (% by mass) of the elements, and an element that is not contained is designated as 0.

[2] The high-strength seamless stainless steel pipe for oil well according to the item [1], wherein the high-strength seamless stainless steel pipe further contains, in addition to the composition, in terms of % by mass, one kind or two kinds selected from

Cu: 0.05-3.0% and
W: 0.05-3.0%.

[3] The high-strength seamless stainless steel pipe for oil well according to the item [1] or [2], wherein the high-strength seamless stainless steel pipe further contains, in addition to the composition, in terms of % by mass, one kind or two or more kinds selected from

Nb: 0.01-0.20%,
Zr: 0.01-0.20%,
B: 0.0005-0.01%,
REM: 0.0005-0.01%,
Ca: 0.0005-0.0025%,
Sn: 0.02-0.20%,
Ta: 0.01-0.1%, and
Mg: 0.002-0.01%.

[4] The high-strength seamless stainless steel pipe for oil well according to any one of the items [1] to [3], wherein the high-strength seamless stainless steel pipe has an average prior austenite grain diameter of 40 μm or less.

Advantageous Effects of Invention

[0017] According to the present invention, a high-strength seamless stainless steel pipe for oil well that is excellent in hot workability, has excellent carbon dioxide gas corrosion resistance, is excellent in SSC resistance under a low temperature environment, and has high strength with a yield strength YS of 655 MPa or more can be obtained.

Description of Embodiments

[0018] The bases of the limitation in composition of the high-strength seamless stainless steel pipe for oil well of the present invention will be described. In the following description, % by mass is shown simply as % unless otherwise indicated.

C: 0.002-0.05%

[0019] C is an important element that increases the strength of the martensitic stainless steel. In the present invention

0.002% or more of C is necessarily contained for securing the target strength. In the case where C is contained in an amount exceeding 0.05%, the strength is rather decreased, and the SSC resistance under a low temperature environment is also deteriorated. Accordingly, in the present invention the C content is 0.002-0.05%. From the standpoint of the carbon dioxide gas corrosion resistance, the C content is preferably 0.03% or less. The C content is more preferably 0.002% or more, more preferably 0.015% or less, further preferably 0.002% or more, and further preferably 0.010% or less.

Si: 0.05-0.50%

[0020] Si is an element that functions as a deoxidizing agent. The effect thereof can be obtained with a Si content of 0.05% or more. With a Si content exceeding 0.50%, the hot workability is deteriorated, and the carbon dioxide gas corrosion resistance is also deteriorated. Accordingly, the Si content is 0.05 to 0.50%. The Si content is preferably 0.10% or more, preferably 0.40% or less, more preferably 0.10% or more, and more preferably 0.30% or less.

Mn: 0.04-1.80%

[0021] Mn is an element that suppresses the formation of δ-ferrite in hot working and enhances the hot workability, and in the present invention, 0.04% or more of Mn is necessarily contained. With an excessive content thereof, the toughness and the SSC resistance under a low temperature environment are adversely affected. Accordingly, the Mn content is in a range of 0.04 to 1.80%. The Mn content is preferably 0.04% or more, preferably 0.80% or less, more preferably 0.05% or more, more preferably 0.50% or less, further preferably 0.05% or more, and further preferably 0.26% or less.

P: 0.030% or less

[0022] P is an element that lowers all the carbon dioxide gas corrosion resistance, pitting corrosion resistance, and the SSC resistance, and the content thereof is desirably decreased as far as possible in the present invention, but excessive decrease thereof may bring about rise in production cost. Accordingly, the P content is 0.030% or less, which is a range that can be practiced industrially inexpensively without significant deterioration of the characteristics. The P content is preferably 0.020% or less.

S: 0.002% or less

[0023] S considerably deteriorates the hot workability, and also deteriorates the SSC resistance under a low temperature environment through the segregation of S on the prior austenite grain boundary and the formation of a Ca based inclusion, and therefore the content of S is desirably decreased as far as possible. With a S content of 0.002% or less, the number density of the Ca based inclusions can be decreased, and the segregation of S on the prior austenite grain boundary can be suppressed, resulting in achieving the target SSC resistance. In view of these factors, the S content is 0.002% or less. The S content is preferably 0.0015% or less.

Cr: 11.0-14.0%

[0024] Cr is an element that forms a protective film to contribute to the enhancement of the corrosion resistance, and 11.0% or more of Cr is necessarily contained in the present invention for securing the corrosion resistance at a high temperature. With a Cr content exceeding 14.0%, the stability of the martensitic phase is deteriorated since residual austenite tends to occur without the martensitic transformation, failing to provide the target strength. Accordingly, the Cr content is 11.0 to 14.0%. The Cr content is preferably 11.5% or more, preferably 13.5% or less, more preferably 12.0% or more, and more preferably 13.0% or less.

Ni: 3.0-6.5%

[0025] Ni is an element that has a function reinforcing the protective film to enhance the corrosion resistance. Ni also increases the strength of the steel through the formation of solid solution therewith. These effects can be obtained with a Ni content of 3.0% or more. With a Ni content exceeding 6.5%, the stability of the martensitic phase is deteriorated since residual austenite tends to occur without the martensitic transformation, resulting in decrease the strength. Accordingly, the Ni content is 3.0 to 6.5%. The Ni content is preferably 5.0% or more, and preferably 6.0% or less.

Mo: 0.5-3.0%

[0026] Mo is an element that increases the resistance against pitting corrosion by Cl^- and low pH, and 0.5% or more of Mo is necessarily contained in the present invention. With a Mo content of less than 0.5%, the corrosion resistance under a severe corrosive environment is deteriorated. With a Mo content exceeding 3.0%, the hot workability and the corrosion resistance are deteriorated through the formation of δ-ferrite. Accordingly, the Mo content is 0.5 to 3.0%. The Mo content is preferably 0.5% or more, preferably 2.5% or less, more preferably 1.5% or more, and more preferably 2.3% or less.

Al: 0.005-0.10%

[0027] Al is an element that functions as a deoxidizing agent. The effect thereof can be obtained with an Al content of 0.005% or more. With an Al content exceeding 0.10%, the toughness is adversely affected since the oxide amount becomes too large. Accordingly, the Al content is 0.005 to 0.10%. The Al content is preferably 0.01% or more, and preferably 0.03% or less.

V: 0.005-0.20%

[0028] V is an element that enhances the strength of the steel through precipitation strengthening. The effect thereof can be obtained with a V content of 0.005% or more. With a V content exceeding 0.20%, the low temperature roughness is deteriorated. Accordingly, the V content is 0.005 to 0.20%. The V content is preferably 0.03% or more, and preferably 0.08% or less.

Ti: 0.01-0.20%

[0029] Ti is an element that forms TiN, and enhances the SSC resistance under a low temperature environment by covering the oxide based or sulfide based inclusion with the TiN. For providing the effect, the Ti content is necessarily 0.01% or more. With a Ti content exceeding 0.20%, the effect is saturated. Accordingly, the Ti content is 0.01 to 0.20%. The Ti content is preferably 0.03% or more, preferably 0.20% or less, more preferably 0.05% or more, and more preferably 0.15% or less.

Co: 0.01-1.0%

[0030] Co is an element that decreases the residual austenite fraction through increase of the Ms point, and enhances the strength and the SSC resistance. The effect can be obtained with a Co content of 0.01% or more. With a Co content exceeding 1.0%, the hot workability is deteriorated. Accordingly, the Co content is 0.01 to 1.0%. The Co content is preferably 0.05% or more, and preferably 0.15% or less. The Co content is more preferably 0.05% or more, and more preferably 0.09% or less.

N: 0.002-0.15%

[0031] N is an element that significantly enhances the pitting corrosion resistance. The effect can be obtained with a N content of 0.002% or more. With a N content exceeding 0.15%, the low temperature toughness is deteriorated. Accordingly, the N content is 0.002 to 0.15%. The N content is preferably 0.002% or more, and preferably 0.015% or less. The N content is more preferably 0.003% or more, and more preferably 0.008% or less.

O (oxygen): 0.010% or less

[0032] O (oxygen) exists in the form of oxides in the steel, and adversely affects the various characteristics. Accordingly, O is desirably decreased as far as possible. In particular, with an O content exceeding 0.010%, both the hot workability and the SSC resistance at a low temperature are significantly deteriorated. Accordingly, the O content is 0.010% or less. The O content is preferably 0.006% or less. The O content is more preferably 0.004% or less.

[0033] In the present invention, Cr, Ni, Mo, Cu, and C are contained in the aforementioned ranges, and simultaneously contained to satisfy the following expression (1).

$$\mathrm{Cr}+0.65\mathrm{Ni}+0.6\mathrm{Mo}+0.55\mathrm{Cu}-20\mathrm{C} \geq 15.0 \qquad (1)$$

wherein Cr, Ni, Mo, Cu, and C represent the contents (% by mass) of the elements, and an element that is not contained is designated as 0.

[0034] In the case where the left-hand value of the expression (1) is less than 15.0, the carbon dioxide gas corrosion resistance under a high temperature corrosive environment at a high temperature of 150°C or more containing CO_2 and Cl^- is deteriorated. Accordingly, in the present invention, Cr, Ni, Mo, Cu, and C are contained to satisfy the expression (1).

[0035] In the present invention, furthermore, Cr, Mo, Si, C, Mn, Ni, Cu, and N are contained to satisfy the following expression (2).

[0036] $Cr+Mo+0.3Si-43.3C-0.4Mn-Ni-0.3Cu-9N \leq 11.0$ (2) wherein Cr, Mo, Si, C, Mn, Ni, Cu, and N represent the contents (% by mass) of the elements, and an element that is not contained is designated as 0.

[0037] In the case where the left-hand value of the expression (2) exceeds 11.0, the hot workability that is necessary and sufficient for producing the seamless stainless steel pipe cannot be obtained, deteriorating the productivity of the steel pipe. Accordingly, in the present invention, Cr, Mo, Si, C, Mn, Ni, Cu, and N are contained to satisfy the expression (2) .

[0038] In the present invention, furthermore, the number density of an inclusion having a major axis of 5 μm or more and $0.5 < Ti/(Ti+Al+Mg+Ca) < 1.0$ is 0.5 per mm^2 or more and 3 per mm^2 or less. In the case where the number density of an inclusion having a major axis of 5 μm or more and $0.5 < Ti/(Ti+Al+Mg+Ca) < 1.0$ is less than 0.5 per mm^2, the amount of the inclusion that is not covered with TiN is increased to become pitting corrosion as the initiation site of SSC, and thus the target SSC resistance under a low temperature environment cannot be obtained. In the case where the number density of an inclusion having $0.5 < Ti/(Ti+Al+Mg+Ca) < 1.0$ exceeds 3 per mm^2, the size of the inclusion is increased associated with the increase of the number density of the inclusion, which rather becomes the initiation site of pitting corrosion, and thus the target SSC resistance under a low temperature environment cannot be obtained. In $0.5 < Ti/(Ti+Al+Mg+Ca) < 1.0$, Ti, Al, Mg, and Ca represent the contents (% by mass) of the elements in the inclusion, and an element that is not contained is designated as 0.

[0039] The inclusion that has a major axis of 5 μm or more is targeted since the inclusion that has a major axis of 5 μm or more tends to become the initiation site of pitting corrosion.

[0040] In the present invention, the balance except for the aforementioned components is Fe and unavoidable impurities.

[0041] While the aforementioned components are the basic components, one kind or two kinds selected from Cu: 0.05-3.0% and W: 0.05-3.0% may be contained as an optional element depending on necessity in addition to the basic composition. Furthermore, one kind or two or more kinds selected from Nb: 0.01-0.20%, Zr: 0.01-0.20%, B: 0.0005-0.01%, REM: 0.0005-0.01%, Ca: 0.0005-0.0025%, Sn: 0.02-0.20%, Ta: 0.01-0.1%, and Mg: 0.002-0.01% may also be contained.

Cu: 0.05-3.0%

[0042] Cu is an element that reinforces the protective film to enhance the corrosion resistance, and may be contained depending on necessity. The effect can be obtained with a Cu content of 0.05% or more. With a Cu content exceeding 3.0%, the grain boundary precipitation of CuS occurs to deteriorate the hot workability. Accordingly, in the case where Cu is contained, the Cu content is 0.05 to 3.0%. The Cu content is preferably 0.5% or more, and preferably 2.5% or less. The Cu content is more preferably 0.5% or more, and more preferably 1.1% or less.

W: 0.05-3.0%

[0043] W is an element that contributes to the enhancement of the strength, and may be contained depending on necessity. The effect can be obtained with a W content of 0.05% or more. With a W content exceeding 3.0%, the effect is saturated. Accordingly, in the case where W is contained, the W content is 0.05 to 3.0%. The W content is preferably 0.5% or more, and preferably 1.5% or less.

Nb: 0.01-0.20%

[0044] Nb is an element that enhances the strength, and may be contained depending on necessity. The effect can be obtained with a Nb content of 0.01% or more. With a Nb content exceeding 0.20%, the effect is saturated. Accordingly, in the case where Nb is contained, the Nb content is 0.01 to 0.20%. The Nb content is preferably 0.05% or more, and preferably 0.15% or less. The Nb content is more preferably 0.07% or more, and more preferably 0.13% or less.

Zr: 0.01-0.20%

[0045] Zr is an element that contributes to the enhancement of the strength, and may be contained depending on necessity. The effect can be obtained with a Zr content of 0.01% or more. With a Zr content exceeding 0.20%, the effect is saturated. Accordingly, in the case where Zr is contained, the Zr content is 0.01 to 0.20%.

B: 0.0005-0.01%

[0046] B is an element that contributes to the enhancement of the strength, and may be contained depending on necessity. The effect can be obtained with a B content of 0.0005% or more. With a B content exceeding 0.01%, the hot workability is deteriorated. Accordingly, in the case where B is contained, the B content is 0.0005 to 0.01%.

REM: 0.0005-0.01%

[0047] A REM is an element that contributes to the improvement of the corrosion resistance, and may be contained depending on necessity. The effect can be obtained with a REM content of 0.0005% or more. With a REM content exceeding 0.01%, the effect is saturated, and the effect corresponding to the content cannot be expected, which is economically disadvantageous. Accordingly, in the case where a REM is contained, the REM content is 0.0005 to 0.01%.

Ca: 0.0005-0.0025%

[0048] Ca is an element that contributes to the improvement of the hot workability, and may be contained depending on necessity. The effect can be obtained with a Ca content of 0.0005% or more. With a Ca content exceeding 0.0025%, the number density of coarse Ca based inclusions is increased, and the target SSC resistance under a low temperature environment cannot be obtained. Accordingly, in the case where Ca is contained, the Ca content is 0.0005 to 0.0025%.

Sn: 0.02-0.20%

[0049] Sn is an element that contributes to the improvement of the corrosion resistance, and may be contained depending on necessity. The effect can be obtained with a Sn content of 0.02% or more. With a Sn content exceeding 0.20%, the effect is saturated, and the effect corresponding to the content cannot be expected, which is economically disadvantageous. Accordingly, in the case where Sn is contained, the Sn content is 0.02 to 0.20%.

Ta: 0.01-0.1%

[0050] Ta is an element that enhances the strength, and also has an effect of improving the sulfide stress cracking resistance. Ta is an element that exerts the similar effect as Nb, and a part of Nb may be replaced by Ta. The effect can be obtained with a Ta content of 0.01% or more. With a Ta content exceeding 0.1%, the toughness is deteriorated. Accordingly, in the case where Ta is contained, the Ta content is 0.01 to 0.1%.

Mg: 0.002-0.01%

[0051] Mg is an element that enhances the corrosion resistance, and may be contained depending on necessity. The effect can be obtained with a Mg content of 0.002% or more. With a Mg content exceeding 0.01%, the effect is saturated, and the effect corresponding to the content cannot be expected. Accordingly, in the case where Mg is contained, the Mg content is 0.002 to 0.01%.

[0052] The high-strength seamless stainless steel pipe for oil well of the present invention has a martensitic phase (tempered martensitic phase) as a main phase for securing the target strength. The balance except for the main phase contains at least one kind of a residual austenitic phase and a ferrite phase. The main phase referred herein means a phase having a volume ratio (area ratio) of 45% or more.

[0053] In the present invention, the average prior austenite grain diameter is preferably 40 μm or less from the standpoint of the achievement of the target SSC resistance under a low temperature environment.

[0054] In the present invention, the number density of an inclusion having a major axis of 5 μm or more and $0.5 < Ti/(Ti+Al+Mg+Ca) < 1.0$ and the prior austenite grain diameter may be measured by the methods shown in the examples described later.

[0055] A preferred production method of the high-strength seamless stainless steel pipe for oil well of the present invention will be described.

[0056] In the present invention, a material for steel pipe having the aforementioned composition is used as a starting material. The production method of the material for steel pipe as the starting material is not particularly limited, and a generally known production method of a seamless steel pipe may be applied. It is preferred that a molten steel having the composition is manufactured by an ordinary manufacturing method, such as a converter furnace, and formed into a material for steel pipe, such as a billet, by an ordinary method, such as a continuous casting method or an ingot-bloom rolling method. The number density of an inclusion having $0.5 < Ti/(Ti+Al+Mg+Ca) < 1.0$ can be controlled to the target value, for example, by measuring the oxygen amount, and changing the amounts of Ti and N added corresponding to the measured value, in the steel manufacturing process.

[0057] Subsequently, the material for steel pipe is heated and formed into a pipe through hot working using a pipe production process by the Mannesmann plug mill process or the Mannesmann mandrel mill process, which is a generally known pipe production method, so as to provide a seamless steel pipe having the aforementioned composition with a target dimension. A seamless steel pipe may also be produced by hot extrusion by a pressing process. The seamless steel pipe after production is preferably cooled to room temperature at a cooling rate of air cooling or larger. According to the procedure, a steel pipe structure having a martensitic phase as a main phase can be secured. For decreasing the average prior austenite grain diameter, the pipe is preferably produced under condition with a ratio (cross sectional area of steel pipe after production) / (cross sectional area of material for steel pipe) of 0.20 or less. The pipe is also preferably produced under condition with a ratio (cross sectional area of steel pipe after production)/(cross sectional area of steel pipe after piercing) of 0.40 or less.

[0058] Subsequent to the cooling to room temperature at a cooling rate of air cooling or larger after the pipe production, in the present invention, the steel pipe is subjected to a quenching treatment by reheating to the Ac_3 transformation point or more, preferably a temperature of 800°C or more, preferably retaining for 5 minutes or more, and then cooling to a temperature of 100°C or less at a cooling rate of air cooling or larger. According to the procedure, a fine martensitic phase and high strength can be achieved. The heating temperature in the quenching treatment is preferably 800 to 950°C from the standpoint of the prevention of coarsening of the structure.

[0059] The "cooling rate of air cooling or larger" herein means 0.01°C/s or more.

[0060] The steel pipe subjected to the quenching treatment is then subjected to a tempering treatment. The tempering treatment may be a treatment of heating to a temperature (tempering temperature) of 500°C or more and less than the Ac_1 transformation point, retaining for a prescribed period of time, preferably 10 minutes or more, and then air cooling. In the case where the tempering temperature is the Ac_1 transformation point or more, a fresh martensitic phase is precipitated after tempering, and the target high strength cannot be secured. Accordingly, the tempering temperature is more preferably 500°C or more and less than the Ac_1 transformation point. According to the procedure, the structure becomes a structure having a tempered martensitic phase as a main phase, and a seamless steel pipe having the target strength and the target corrosion resistance can be obtained.

[0061] The operation of the quenching and the tempering is preferably repeated twice or more from the standpoint of the reduction of the average prior austenite grain diameter.

[0062] The Ac_3 transformation point and the Ac_1 transformation point above are actual measured values read from the change in expansion coefficient (linear expansion coefficient) in heating and cooling a test specimen (3 mm in diameter × 10 mm in length) at a rate of 15°C/min.

[0063] While the example of a seamless steel pipe has been described above, the present invention is not limited thereto. An electric resistance welded steel pipe or an UOE steel pipe may be produced according to the ordinary process by using the material for steel pipe having the aforementioned composition, so as to provide a steel pipe for oil well.

Examples

[0064] The present invention will be described with reference to examples below.

[0065] The molten steels having the compositions shown in Table 1 each were manufactured, cast into a material for steel pipe, and formed into a pipe through hot working using a model seamless mill, and the manufactured pipe was cooled to provide a seamless steel pipe having an outer diameter of 83.8 mm and a thickness of 12.7 mm. For the steel pipe No. 13, in order to control the number of the inclusion having a major axis of 5 μm or more and $0.5 < Ti/(Ti+Al+Mg+Ca) < 1.0$ to more than 3 per mm^2, the oxygen amount was measured online in the steel manufacturing process, and the amounts of Ti and N added were changed corresponding to the measured value, so as to control the number thereof. For the steel pipe No. 14, in order to control the number of the inclusion having a major axis of 5 μm or more and $0.5 < Ti/(Ti+Al+Mg+Ca) < 1.0$ to less than 0.5 per mm^2, the oxygen amount was measured online in the steel manufacturing process, and the amounts of Ti and N added were changed corresponding to the measured value, so as to control the number thereof.

[0066] Subsequently, a material test specimen was cut out from the resulting seamless steel pipe, and subjected to a quenching treatment by heating to a heating temperature (reheating temperature) for a soaking time shown in Table 2, and then air cooling to a cooling termination temperature shown in Table 2. Furthermore, the material test specimen was subjected to a tempering treatment by heating to a tempering temperature for a soaking time shown in Table 2, and then air cooling.

[0067] An API (American Petroleum Institute) arc-shaped tensile test specimen was cut out from the material test specimen having been subjected to the quenching treatment and the tempering treatment, and subjected to a tensile test according to the regulation of API, so as to measure the tensile characteristics (i.e., the yield strength YS and the tensile strength TS). A specimen that had a yield strength YS of 655 MPa or more was designated as pass, and a specimen that had a yield strength YS of less than 655 MPa designated as fail.

[0068] A corrosion test specimen of 3 mm in thickness × 30 mm in width × 40 mm in length was produced through machining from the material test specimen having been subjected to the quenching treatment and the tempering treatment, and subjected to a corrosion test.

[0069] The corrosion test was performed by immersing the test specimen in a test solution, i.e., a 20% by mass NaCl aqueous solution (solution temperature: 150°C, CO_2 gas atmosphere of 10 atm), retained in an autoclave, for an immersion time of 14 days. The test specimen after the test was measured for the weight, and the corrosion rate was calculated from the weight reduction before and after the corrosion test. A specimen that had a corrosion rate of 0.125 mm/y or less was designated as pass, and a specimen that had a corrosion rate exceeding 0.125 mm/y was designated as fail.

[0070] The test specimen after the corrosion test was observed with a magnifying glass having a magnification of 10 for the presence or absence of occurrence of pitting corrosion on the surface of the test specimen. Pitting corrosion with a diameter of 0.2 mm or more was designated as presence. A specimen that had no occurrence of pitting corrosion was designated as pass, and a specimen that had the presence of pitting corrosion was designated as fail.

[0071] An SSC test was performed according to NACE TM0177Method A. The test environment used was an aqueous solution obtained by adding Na acetate and hydrochloric acid to a 25% by mass NaCl aqueous solution (liquid temperature: 4°C, H_2S: 0.1 bar, CO_2: 0.9 bar) to provide pH 4.5. The test was performed with an immersion time of 720 hours and a load stress of 90% of the yield stress. A test specimen after the test that had no crack occurring was designated as pass (no in Table 3), and a test specimen that had a crack occurring was designated as fail (yes in Table 3).

[0072] For evaluating the hot workability, a smooth test specimen in a round bar shape having a diameter of parallel portion of 10 mm was used, and with a Greeble tester, was heated to 1,250°C, and after retaining for 100 seconds, cooled to 1,000°C at 1°C/sec, and after retaining for 10 seconds, strained until fracture, and the decrease rate of cross section was measured. The case where the decrease rate of cross section was 70% or more was assumed to achieve excellent hot workability and designated as pass. The case where the decrease rate of cross section was less than 70% was designated as fail.

[0073] For the number of the inclusions, as a specimen at an arbitrary one position in the circumferential direction at the end of the steel pipe for observing the cross section perpendicular to the pipe thickness direction with a scanning electron microscope (SEM), a region of 500 mm^2 was collected at each of the position at 1/4 of the thickness and the position at 3/4 of the thickness from the outer surface of the pipe. For each of the specimens thus collected, the inclusion was identified by SEM observation, and analyzed for the chemical composition thereof by the characteristic X-ray analyzer attached to the SEM. The inclusion having $0.5 < Ti/(Ti+Al+Mg+Ca) < 1.0$ was calculated, and the number of the inclusion per unit area was calculated. The inclusion having a major axis of 5 μm or more was discriminated by defining the outer periphery of the inclusion through binarization of the contrast of the backscattered electron image by the scanning electron microscope, and measuring the major axis from the outer periphery of the inclusion.

[0074] A specimen for measuring the average prior austenite grain diameter was collected from an arbitrary one position in the circumferential direction at the end of the steel pipe from the cross section perpendicular to the longitudinal direction of the pipe at the position at 1/2 of the thickness from the outer surface of the pipe. The specimen thus collected was observed by EBSD, and then the prior austenite grains were reconstructed from the EBSD observation data by using a reverse analysis software for prior austenite grans. On the resulting reconstructed image of prior austenite grains, three straight lines of 300 μm were drawn in the circumferential direction of the pipe with a distance of 500 μm, and the average prior austenite grain diameter was measured by the section method.

[0075] The results obtained are shown in Table 3.

Table 1

Steel species No.	Com position (% by mass)																	Note
	C	Si	Mn	P	S	Cr	Ni	Mo	Al	V	Ti	Co	N	O	Left-hand value of expression (1) *1	Left-hand value of expression (2) *2	Cu, W	Nb, Zr, B, REM, Ca, Sn, Ta, Mg	
A	0.0070	0.16	0.70	0.006	0.0010	13.3	6.0	1.4	0.021	0.022	0.079	0.069	0.0109	0.0033	17.9	7.8	Cu: 0.92	Zr: 0.02, REM: 0.004	Inventive steel
B	0.0110	0.18	0.72	0.012	0.0007	12.0	4.6	2.2	0.029	0.009	0.087	0.063	0.0065	0.0027	16.1	8.8		Zr: 0.02, Ta: 0.03, Ca: 0.0023, Mg: 0.003	Inventive steel
C	0.0130	0.17	1.54	0.011	0.0007	11.8	5.1	1.9	0.033	0.012	0.101	0.035	0.0057	0.0027	16.0	7.4		-	Inventive steel
D	0.0100	0.17	0.32	0.016	0.0011	11.9	5.3	1.9	0.028	0.042	0.061	0.275	0.0047	0.0026	16.3	7.9	Cu: 0.19	-	Inventive steel
E	0.0090	0.21	0.15	0.013	0.0009	11.8	5.8	2.0	0.043	0.050	0.053	0.239	0.0055	0.0035	16.6	7.5	Cu: 0.25	-	Inventive steel
F	0.0102	0.21	0.34	0.019	0.0009	12.7	5.8	2.4	0.043	0.017	0.115	0.103	0.0070	0.0036	17.7	8.7	Cu: 0.06	-	Inventive steel
G	0.0098	0.19	0.29	0.017	0.0008	11.6	5.7	2.0	0.033	0.035	0.073	0.138	0.0076	0.0038	16.3	7.3	Cu: 0.16	B: 0.003	Inventive steel
H	0.0130	0.19	0.40	0.012	0.0010	13.9	6.5	2.1	0.035	0.036	0.058	0.136	0.0050	0.0029	19.1	8.5	Cu: 0.94	Nb: 0.013, Ca: 0.0020	Inventive steel
I	0.0112	0.25	0.44	0.014	0.0008	11.7	5.0	2.1	0.031	0.015	0.111	0.384	0.0118	0.0028	16.0	8.0	Cu: 0.33	-	Inventive steel
J	0.0157	0.18	0.34	0.013	0.0010	13.5	4.3	1.4	0.040	0.050	0.066	0.396	0.0064	0.0036	16.8	9.7	Cu: 0.24	-	Inventive steel

(continued)

Steel species No.	Com position (% by mass)																	Note
	C	Si	Mn	P	S	Cr	Ni	Mo	Al	V	Ti	Co	N	O	Left-hand value of expression (1) *1	Left-hand value of expression (2) *2	Cu, W	Nb, Zr, B, REM, Ca, Sn, Ta, Mg	
K	0.0094	0.22	0.37	0.015	0.0012	12.3	6.3	2.8	0.041	0.018	0.125	0.185	0.0076	0.0030	17.9	8.2	Cu: 0.18	Nb: 0.01, Sn: 0.068	Inventive steel
L	0.0128	0.22	0.32	0.013	0.0009	13.1	5.6	1.7	0.039	0.036	0.046	0.360	0.0047	0.0030	17.5	8.4	Cu: 0.45	-	Inventive steel
M	0.0144	0.20	0.29	0.016	0.0012	11.3	4.7	2.5	0.035	0.013	0.111	0.299	0.0066	0.0036	15.6	8.2	Cu: 0.47	Ca: 0.0010	Inventive steel
N	0.0221	0.16	0.51	0.015	0.0009	11.9	5.0	2.5	0.048	0.039	0.139	0.214	0.0168	0.0032	16.2	8.0	Cu: 0.39	-	Inventive steel
O	0.0142	0.21	0.40	0.013	0.0012	12.0	6.4	2.8	0.048	0.067	0.166	0.518	0.0114	0.0027	17.6	7.6		-	Inventive steel
P	0.0128	0.17	1.46	0.013	0.0009	12.4	4.8	1.9	0.033	0.010	0.099	0.030	0.0063	0.0028	16.4	8.4	W: 0.56	-	Inventive steel
Q	0.0097	0.17	0.47	0.016	0.0009	11.6	5.2	1.8	0.043	0.024	0.104	0.168	0.0055	0.0030	15.9	7.3	Cu: 0.94	Nb: 0.06	Inventive steel
R	0.0645	0.27	0.37	0.009	0.0011	16.7	7.2	1.5	0.018	0.046	0.000	0.069	0.0970	0.0036	21.0	7.3		-	Comparative steel
S	0.0266	0.34	0.36	0.024	0.0011	17.2	6.9	1.6	0.010	0.102	0.000	0.050	0.0374	0.0031	22.1	10.4		-	Comparative steel
T	0.0210	0.27	0.45	0.020	0.0011	14.5	4.1	1.8	0.010	0.045	0.000	0.044	0.0711	0.0010	17.8	10.6		-	Comparative steel
U	0.0271	0.14	0.84	0.014	0.0012	11.8	4.4	0.7	0.030	0.008	0.000	0.064	0.0082	0.0028	14.5	6.6		-	Comparative steel
V	0.0573	0.26	0.35	0.009	0.0008	17.2	5.9	1.6	0.021	0.036	0.193	0.047	0.1152	0.0036	20.8	9.1	Cu: 0.81	-	Comparative steel

(continued)

Steel species No.	Com position (% by mass)																	Note
	C	Si	Mn	P	S	Cr	Ni	Mo	Al	V	Ti	Co	N	O	Left-hand value of expression (1) *1	Left-hand value of expression (2) *2	Cu, W	Nb, Zr, B, REM, Ca, Sn, Ta, Mg	
W	0.0138	0.17	0.80	0.013	0.0011	11.7	4.1	0.7	0.029	0.009	0.122	0.061	0.0072	0.0030	14.5	7.4		-	Comparative steel
X	0.0182	0.18	0.27	0.013	0.0011	11.1	4.8	2.4	0.041	0.023	0.238	0.071	0.0071	0.0027	15.3	7.8	Cu: 0.09	Ca: 0.0018	Comparative steel
Y	0.0109	0.15	0.39	0.016	0.0010	11.5	6.3	2.6	0.042	0.017	0.074	1.176	0.0127	0.0027	16.9	6.9	Cu: 0.70	-	Comparative steel
Z	0.0434	0.21	0.25	0.014	0.0008	10.5	4.7	2.8	0.035	0.012	0.235	0.288	0.0044	0.0038	14.4	6.6	Cu: 0.06	-	Comparative steel
AA	0.0132	0.16	1.68	0.009	0.0010	11.9	5.1	2.2	0.032	0.010	0.103	0.000	0.0081	0.0036	16.3	7.7		-	Comparative steel
AB	0.0091	0.15	1.52	0.012	0.0008	12.0	4.4	1.9	0.033	0.010	0.083	0.029	0.0081	0.0171	15.8	8.5		-	Comparative steel
AC	0.0178	0.26	0.46	0.024	0.0012	14.8	3.9	1.9	0.009	0.051	0	0.042	0.0829	0.0011	18.1	11.2		-	Comparative steel

Underlined value: outside the scope of invention

*1) Cr+0.65Ni+0.6Mo+0.55Cu-20C

*2) Cr+Mo+0.3Si-43.3C-0.4Mn-Ni-0.3Cu-9N

Table 2

Steel pipe No.	Steel species No.	Dimension of steel pipe		Cross section ratio		Heat treatment (first)							Heat treatment (second)						
						Quenching				Tempering			Quenching				Tempering		
		Outer diameter (mm)	Thickness (mm)	After production of pipe/material for steel pipe	After production of pipe/after piercing	Heating temperature (°C)	Soaking time (min)	Cooling	Cooling termination temperature (°C)	Tempering temperature (°C)	Soaking time (min)	Cooling	Heating temperature (°C)	Soaking time (min)	Cooling	Cooling termination temperature (°C)	Tempering temperature (°C)	Soaking time (min)	Cooling
1	A	88.9	6.45	0.059	0.157	810	20	Air cooling	25	600	40	Air cooling	-	-	-	-	-	-	-
2	A	88.9	6.45	0.059	0.157	810	20	Air cooling	25	600	40	Air cooling	810	20	Air cooling	25	600	40	Air cooling
3	B	101.6	15.49	0.148	0.300	810	20	Air cooling	25	600	40	Air cooling	-	-	-	-	-	-	-
4	B	101.6	15.49	0.148	0.300	810	20	Air cooling	25	600	40	Air cooling	810	20	Air cooling	25	600	40	Air cooling
5	C	73.02	11.18	0.077	0.166	810	20	Air cooling	25	550	40	Air cooling	-	-	-	-	-	-	-
6	D	114.3	12.7	0.143	0.296	920	20	Water cooling	25	595	60	Air cooling	-	-	-	-	-	-	-
7	E	88.9	6.45	0.059	0.157	920	20	Air cooling	25	605	60	Air cooling	-	-	-	-	-	-	-
8	F	101.6	15.49	0.148	0.300	920	20	Water cooling	25	550	30	Air cooling	-	-	-	-	-	-	-

(continued)

Steel pipe No.	Steel species No.	Dimension of steel pipe		Cross section ratio		Heat treatment (first)							Heat treatment (second)						
						Quenching				Tempering			Quenching				Tempering		
		Outer diameter (mm)	Thickness (mm)	After production of pipe/material for steel pipe	After production of pipe/after piercing	Heating temperature (°C)	Soaking time (min)	Cooling	Cooling termination temperature (°C)	Tempering temperature (°C)	Soaking time (min)	Cooling	Heating temperature (°C)	Soaking time (min)	Cooling	Cooling termination temperature (°C)	Tempering temperature (°C)	Soaking time (min)	Cooling
9	G	73.02	11.18	0.077	0.166	920	20	Air cooling	25	510	30	Air cooling	-	-	-	-	-	-	-
10	H	114.3	12.7	0.143	0.296	900	20	Water cooling	25	600	30	Air cooling	-	-	-	-	-	-	-
11	I	88.9	6.45	0.059	0.157	920	20	Air cooling	25	565	60	Air cooling	-	-	-	-	-	-	-
12	J	101.6	15.49	0.148	0.300	810	20	Air cooling	25	595	45	Air cooling	-	-	-	-	-	-	-
13	K	73.02	11.18	0.077	0.166	900	20	Water cooling	25	575	30	Air cooling	-	-	-	-	-	-	-
14	L	114.3	12.7	0.143	0.296	810	20	Air cooling	25	600	60	Air cooling	-	-	-	-	-	-	-
15	M	88.9	6.45	0.059	0.157	900	20	Water cooling	25	585	60	Air cooling	-	-	-	-	-	-	-
16	N	101.6	15.49	0.148	0.300	920	20	Water cooling	25	590	60	Air cooling	-	-	-	-	-	-	-

(continued)

Steel pipe No.	Steel species No.	Dimension of steel pipe		Cross section ratio		Heat treatment (first)							Heat treatment (second)						
						Quenching				Tempering			Quenching				Tempering		
		Outer diameter (mm)	Thickness (mm)	After production of pipe/material for steel pipe	After production of pipe/after piercing	Heating temperature (°C)	Soaking time (min)	Cooling	Cooling termination temperature (°C)	Tempering temperature (°C)	Soaking time (min)	Cooling	Heating temperature (°C)	Soaking time (min)	Cooling	Cooling termination temperature (°C)	Tempering temperature (°C)	Soaking time (min)	Cooling
17	O	73.02	11.18	0.077	0.166	920	20	Water cooling	25	580	45	Air cooling	-	-	-	-	-	-	-
18	O	73.02	11.18	0.141	0.450	920	20	Water cooling	25	580	45	Air cooling	-	-	-	-	-	-	-
19	P	114.3	12.7	0.143	0.296	810	20	Air cooling	25	550	40	Air cooling	-	-	-	-	-	-	-
20	P	114.3	12.7	0.263	0.296	810	20	Air cooling	25	550	40	Air cooling	-	-	-	-	-	-	-
21	Q	88.9	6.45	0.059	0.157	810	20	Water cooling	25	525	30	Air cooling	-	-	-	-	-	-	-
22	Q	88.9	6.45	0.059	0.157	950	20	Water cooling	25	525	30	Air cooling	-	-	-	-	-	-	-
23	R	88.9	6.45	0.059	0.157	920	20	Air cooling	30	580	20	Air cooling	-	-	-	-	-	-	-
24	S	101.6	15.49	0.148	0.300	920	20	Air cooling	30	580	20	Air cooling	-	-	-	-	-	-	-

(continued)

Steel pipe No.	Steel species No.	Dimension of steel pipe		Cross section ratio		Heat treatment (first)							Heat treatment (second)						
						Quenching				Tempering			Quenching				Tempering		
		Outer diameter (mm)	Thickness (mm)	After production of pipe/material for steel pipe	After production of pipe/after piercing	Heating temperature (°C)	Soaking time (min)	Cooling	Cooling termination temperature (°C)	Tempering temperature (°C)	Soaking time (min)	Cooling	Heating temperature (°C)	Soaking time (min)	Cooling	Cooling termination temperature (°C)	Tempering temperature (°C)	Soaking time (min)	Cooling
25	T	73.02	11.18	0.077	0.166	910	20	Air cooling	30	530	20	Air cooling	-	-	-	-	-	-	-
26	U	114.3	12.7	0.143	0.296	810	20	Air cooling	25	600	40	Air cooling	-	-	-	-	-	-	-
27	V	88.9	6.45	0.059	0.157	920	20	Air cooling	30	580	20	Air cooling	-	-	-	-	-	-	-
28	W	101.6	15.49	0.148	0.300	810	20	Air cooling	25	600	40	Air cooling	-	-	-	-	-	-	-
29	X	73.02	11.18	0.077	0.166	810	20	Air cooling	25	560	45	Air cooling	-	-	-	-	-	-	-
30	Y	114.3	12.7	0.143	0.296	920	20	Water cooling	25	585	30	Air cooling	-	-	-	-	-	-	-
31	Z	88.9	6.45	0.059	0.157	810	20	Air cooling	25	570	60	Air cooling	-	-	-	-	-	-	-
32	AA	101.6	15.49	0.148	0.300	810	20	Air cooling	25	550	40	Air cooling	-	-	-	-	-	-	-

(continued)

		Dimension of steel pipe		Cross section ratio		Heat treatment (first)							Heat treatment (second)						
						Quenching				Tempering			Quenching				Tempering		
Steel pipe No.	Steel species No.	Outer diameter (mm)	Thickness (mm)	After production of pipe/ material for steel pipe	After production of pipe/after piercing	Heating temperature (°C)	Soaking time (min)	Cooling	Cooling termination temperature (°C)	Tempering temperature (°C)	Soaking time (min)	Cooling	Heating temperature (°C)	Soaking time (min)	Cooling	Cooling termination temperature (°C)	Tempering temperature (°C)	Soaking time (min)	Cooling
33	AB	73.02	11.18	0.077	0.166	810	20	Air cooling	25	550	40	Air cooling	-	-	-	-	-	-	-
34	AC	73.02	11.18	0.077	0.166	910	20	Air cooling	30	530	20	Air cooling	-	-	-	-	-	-	-

Underlined value: outside the scope of invention

Table 3

Steel pipe No.	Steel species No.	Inclusions having major axis of 5 μm or more and 0.5 < Ti/(Ti+Al+Mg+Ca) < 1.0	Average prior austenite grain diameter	Hot workability	Tensile characteristics		Corrosion characteristics		SSC	Note
		per mm^2	μm	Decrease rate of cross section (%)	Yield strength YS (MPa)	Tensile strength TS (MPa)	Corrosion rate (mm/y)	Pitting corrosion		
1	A	2.7	10.6	72	699	871	0.033	No	No	Invention
2	A	2.9	9.2	72	734	860	0.031	No	No	Invention
3	B	1.5	28.5	76	698	815	0.119	No	No	Invention
4	B	1.5	26.9	76	723	816	0.123	No	No	Invention
5	C	2	12.3	84	813	965	0.119	No	No	Invention
6	D	1.9	27.1	78	828	838	0.096	No	No	Invention
7	E	2.2	9.1	80	789	853	0.083	No	No	Invention
8	F	1.3	28	76	806	888	0.059	No	No	Invention
9	G	1.8	13.1	75	876	922	0.117	No	No	Invention
10	H	2.5	29.9	73	790	831	0.008	No	No	Invention
11	I	1.9	10.7	72	829	880	0.106	No	No	Invention
12	J	1.2	27.7	71	737	809	0.037	No	No	Invention
13	K	4.4	12.9	79	854	873	0.032	No	Yes	Comparison
14	L	0.3	29.7	76	759	878	0.057	No	Yes	Comparison
15	M	1.5	9.8	75	790	879	0.099	No	No	Invention
16	N	2.7	26.2	82	814	878	0.083	No	No	Invention
17	O	1.6	12.9	72	855	900	0.04	No	No	Invention
18	O	1.7	41.4	72	833	836	0.046	No	No	Invention
19	P	2	25.7	78	843	955	0.103	No	No	Invention
20	P	2.8	44.3	78	830	990	0.109	No	No	Invention
21	Q	2.2	10.8	81	861	889	0.065	No	No	Invention
22	Q	1.9	41.9	81	860	866	0.067	No	No	Invention

(continued)

Steel pipe No.	Steel species No.	Inclusions having major axis of 5 μm or more and 0.5 < Ti/(Ti+Al+Mg+Ca) < 1.0	Average prior austenite grain diameter	Hot workability	Tensile characteristics		Corrosion characteristics		SSC	Note
		per mm^2	μm	Decrease rate of cross section (%)	Yield strength YS (MPa)	Tensile strength TS (MPa)	Corrosion rate (mm/y)	Pitting corrosion		
23	R	0	9.8	85	628	891	0.008	No	Yes	Comparison
24	S	0	28.4	77	648	876	0.009	No	Yes	Comparison
25	T	0	12.4	75	631	818	0.019	No	Yes	Comparison
26	U	0	26.6	86	718	848	0.185	Yes	Yes	Comparison
27	V	1.6	10.9	86	644	889	0.008	No	Yes	Comparison
28	W	2.4	28.8	82	672	757	0.265	Yes	No	Comparison
29	X	7.6	12	78	819	877	0.124	No	Yes	Comparison
30	Y	2.2	27.9	62	799	888	0.048	No	No	Comparison
31	Z	8.3	10.7	81	832	924	0.324	Yes	Yes	Comparison
32	AA	2.6	29.4	84	641	915	0.118	No	Yes	Comparison
33	AB	4	12.2	56	830	936	0.113	No	Yes	Comparison
34	AC	0	11.0	63	631	841	0.022	No	No	Comparison
Underlined value: outside the scope of invention										

[0076] All the examples of the invention were excellent in hot workability with a yield strength YS of 655 MPa or more, were excellent in corrosion resistance under a corrosive environment at a high temperature of 150°C or more containing CO_2 and Cl^- (carbon dioxide gas corrosion resistance), were excellent in SSC resistance under a low temperature environment, and had a decrease rate of cross section of 70% or more. On the other hand, in the comparative examples outside the scope of the present invention, the intended value was not obtained in at least one of the yield strength YS, the hot workability, the SSC resistance under a low temperature environment, the corrosion rate, and the decrease rate of cross section.

Claims

1. A high-strength seamless stainless steel pipe for oil well having a composition containing, in terms of % by mass,

C: 0.002-0.05%,
Si: 0.05-0.50%,
Mn: 0.04-1.80%,
P: 0.030% or less,
S: 0.002% or less,
Cr: 11.0-14.0%,
Ni: 3.0-6.5%,
Mo: 0.5-3.0%,
Al: 0.005-0.10%,
V: 0.005-0.20%,
Ti: 0.01-0.20%,
Co: 0.01-1.0%,
N: 0.002-0.15%, and
O: 0.010% or less,
the balance being Fe and unavoidable impurities, and satisfying the following expression (1) and the following expression (2),
having a number density of an inclusion having a major axis of 5 μm or more and $0.5 < Ti/(Ti+Al+Mg+Ca) < 1.0$ of 0.5 per mm^2 or more and 3 per mm^2 or less, and having a yield strength of 655 MPa or more,
wherein in $0.5 < Ti/(Ti+Al+Mg+Ca) < 1.0$, Ti, Al, Mg, and Ca represent the contents (% by mass) of the elements in the inclusion, and an element that is not contained is designated as 0,

$$Cr+0.65Ni+0.6Mo+0.55Cu-20C \geq 15.0 \quad (1)$$

$$Cr+Mo+0.3Si-43.3C-0.4Mn-Ni-0.3Cu-9N \leq 11.0 \quad (2)$$

wherein Cr, Ni, Mo, Cu, C, Si, Mn, and N represent the contents (% by mass) of the elements, and an element that is not contained is designated as 0.

2. The high-strength seamless stainless steel pipe for oil well according to claim 1, wherein the high-strength seamless stainless steel pipe further contains, in addition to the composition, in terms of % by mass, one kind or two kinds selected from

Cu: 0.05-3.0% and
W: 0.05-3.0%.

3. The high-strength seamless stainless steel pipe for oil well according to claim 1 or 2, wherein the high-strength seamless stainless steel pipe further contains, in addition to the composition, in terms of % by mass, one kind or two or more kinds selected from

Nb: 0.01-0.20%,
Zr: 0.01-0.20%,
B: 0.0005-0.01%,
REM: 0.0005-0.01%,
Ca: 0.0005-0.0025%,
Sn: 0.02-0.20%,

Ta: 0.01-0.1%, and
Mg: 0.002-0.01%.

4. The high-strength seamless stainless steel pipe for oil well according to any one of claims 1 to 3, wherein the high-strength seamless stainless steel pipe has an average prior austenite grain diameter of 40 μm or less.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2020/043310

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl. C21D8/10(2006.01)n, C21D9/08(2006.01)i, C22C38/00(2006.01)i, C22C38/58(2006.01)i
FI: C22C38/00302Z, C22C38/58, C21D9/08E, C21D8/10D
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl. C21D8/10, C21D9/08, C22C38/00, C22C38/58

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan	1922-1996
Published unexamined utility model applications of Japan	1971-2021
Registered utility model specifications of Japan	1996-2021
Published registered utility model applications of Japan	1994-2021

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2019/065114 A1 (JFE STEEL CORPORATION) 04 April 2019 (2019-04-04)	1-4
A	WO 2018/181404 A1 (NIPPON STEEL & SUMITOMO METAL CORPORATION) 04 October 2018 (2018-10-04)	1-4
A	JP 2001-131698 A (SUMITOMO METAL INDUSTRIES, LTD.) 15 May 2001 (2001-05-15)	1-4
A	WO 2019/225280 A1 (JFE STEEL CORPORATION) 28 November 2019 (2019-11-28)	1-4
A	WO 2019/225281 A1 (JFE STEEL CORPORATION) 28 November 2019 (2019-11-28)	1-4

☐ Further documents are listed in the continuation of Box C.   ☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search
12 January 2021

Date of mailing of the international search report
26 January 2021

Name and mailing address of the ISA/
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku,
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Form PCT/ISA/210 (second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2020/043310

WO 2019/065114 A1	04 April 2019	AR 113183 A1 BR 112020004793 A2 EP 3690074 A1 US 2020283866 A1
WO 2018/181404 A1	04 October 2018	EP 3604591 A1 CN 110462085 A MX 2019011443 A BR 112019017764 A2 RU 2718019 C1
JP 2001-131698 A	15 May 2001	(Family: none)
WO 2019/225280 A1	28 November 2019	JP 6680408 B1
WO 2019/225281 A1	28 November 2019	CN 112166205 A JP 6680409 B1

Form PCT/ISA/210 (patent family annex) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

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- WO 2008023702 A **[0007]**
- JP 9170019 A **[0007]**
- JP 7166303 A **[0007]**